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The Cationic Polymerization of Methallyl Vinyl Ether

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The polymerization of methallyl vinyl ether was carried out in toluene by means of $BF_3 \cdot OEt_2$. The reaction proceeded through the vinyl double bond, giving a polymer containing one methallyl double bond per monomeric unit. The polymer obtained below $-78°C$ was a white powder and had an isotactic configuration. The molecular weight of the polymer decreased with an increase in the polymerization temperature, and the polymer obtained at 0°C was a viscous liquid. In *n*-heptane, the yields of the polymer decreased and a part of the polymer obtained was insoluble in usual organic solvents, probably because of the cross-linking which occurred during the polymerization reaction. In *n*-heptane - toluene mixtures, the yields were much higher than those in toluene or *n*-heptane alone. The NMR spectra of the polymer were measured in CCl_4, benzene, pyridine, and quinoline at various temperatures in order to investigate the polymer-solvent interaction; the π-complex formation between the monomeric unit of the polymer and the aromatic solvent molecule was suggested.

A number of papers have been published on the stereospecific polymerization of vinyl ethers.[1-6] However, there have been only a few reports[7-9] on the cationic polymerization of vinyl ether with an unsaturated substituent. In a previous work,[9] we studied the polymerization of allyl vinyl ether by $BF_3 \cdot OEt_2$. In the present work we investigated the polymerization of methallyl vinyl ether (MAVE) by $BF_3 \cdot OEt_2$; the polymerization was found to proceed through the vinyl double bond, giving a polymer containing one methallyl double bond per monomeric unit. At low polymerization temperatures, the polymer produced was a white powder with a predominantly isotactic configuration.

Experimental

Reagents. MAVE was prepared from methyl vinyl ether and methallyl alcohol by the vinyl transetherification catalyzed by mercuric acetate in the presence of molecular sieves.[10] The monomer obtained was refluxed over lithium aluminum hydride under a nitrogen atmosphere and was then fractionally distilled. Bp 90.0°C. The purified MAVE was sealed in ampoules under dry nitrogen and was stored at $-20°C$.

The toluene and *n*-heptane were purified in the usual manner, dried, and stored over calcium hydride. They were then dried further with a small amount of *n*-butyllithium and distilled under a high vacuum just before use.

Methylene chloride, nitroethane, and diethyl ether were purified as usual, dried with calcium hydride, and distilled under a high vacuum just before use.

$BF_3 \cdot OEt_2$ was purified by distillation under a reduced nitrogen pressure and was used as a toluene solution.

Nitrogen gas was purified by being passed through a column packed with molecular sieves 4A cooled at $-78°C$ in a dry ice - acetone bath.

Polymerization. A vessel equipped with a three-way stop-cock was flushed with dry nitrogen. The monomer and a solvent were added with hypodermic syringes, and cooled at a given temperature. The polymerization was initiated by introducing the catalyst drop by drop with a syringe, and was stopped by adding a small amount of ammoniac methanol which had been cooled to the same temperature as the reaction mixture. The mixture was then poured into a large amount of methanol containing a small amount of phenyl-β-naphthylamine. The precipitated polymer was collected by filtration, washed throughly with methanol, and dried *in vacuo* at room temperature for three days. The filtrate was concentrated to dryness under a high vacuum. The resultant methanol-soluble fraction was redissolved in benzene to free it from inorganic materials and then dried by the freeze-drying technique. The polymer was stored under reduced nitrogen pressure at $-20°C$ in order to avoid the formation of a cross-linked insoluble polymer.

Measurements of NMR Spectra. The NMR spectra were obtained with a JEOL JNM-4H-100 spectrometer at 100 MHz by using a 10 w/v% solution containing a small amount of tetramethylsilane as an internal standard. The spectra of the polymer and MAVE were measured in carbon tetrachloride at 60°C and in chloroform at 22.5°C respectively. The spectra using a spin-decoupling technique were measured in pyridine at 100°C.

The temperature dependence of the spectrum of the polymer was investigated in several solvents, using hexamethyldisilane as an external standard, in precision coaxial tubing (Wilmad Glass Co.). A correction of the chemical shift involving the difference between the bulk diamagnetic susceptibilities of the reference compound and the sample solution was applied. The volume magnetic susceptibilities, χ_v, were taken from the literature.[11,12] The χ_v value of the neat solvent was used instead of that of the sample solution.

Viscosity Measurements. The solution viscosity of the polymer was measured on its toluene solution (0.7—1.0 g/d*l*) at $30.0 \pm 0.03°C$ using Ostwald's viscometer.

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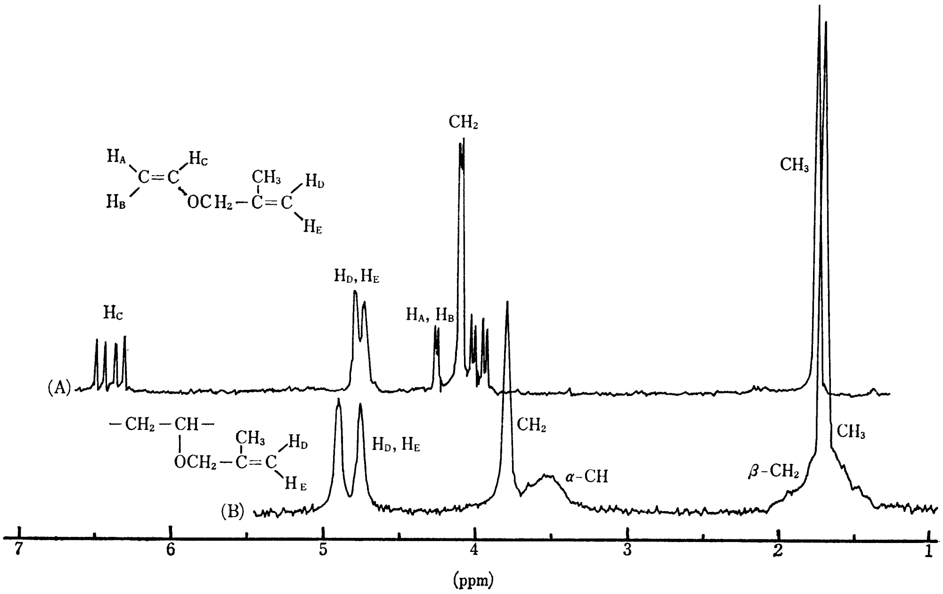

Fig. 1. NMR spectra of methallyl vinyl ether (A) and poly(methallyl vinyl ether) (B) obtained in toluene at −78°C by $BF_3 \cdot OEt_2$

Measurements of Molecular Weight. The molecular weight of the polymer was measured on its benzene solution (10 g/*l*) at 37°C using a Mechrolab 301 A Vapor Pressure Osmometer.

Results and Discussion

Structure and Tacticity of PMAVE. Figure 1 shows the NMR spectrum of PMAVE obtained at −78°C in toluene by $BF_3 \cdot OEt_2$, together with the spectrum of MAVE. The spectrum of the polymer consisted of four groups of peaks, which correspond to the methyl-proton signal overlapping with that of the β-methylene protons, α-methine proton signal, methallyl methylene proton signal, and the terminal methylene proton signals with decreasing magnetic field. The intensity ratio of these groups of peaks was 5.3 : 1.1 : 2.0 : 2.0. There were no resonances due to the protons of the vinyl group, which were observed at about 3.9—4.3 and 6.4 ppm in the spectrum of the MAVE. These facts show that MAVE polymerized exclusively through the vinyl double bond, leaving the methallyl double bond unaffected by the polymerization.

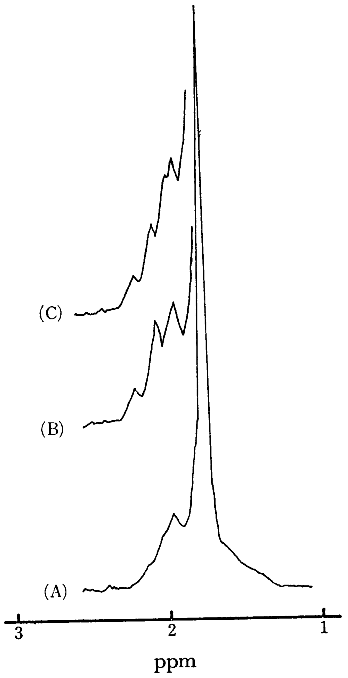

Fig. 2. β-Methylene and methyl protons resonances of PMAVE obtained in toluene at −78°C (20 w/v% pyridine solution, 100°C).
A: Undecoupled.
B: Decoupled from α-methine proton.
C: PMAVE obtained in toluene at 0°C. Decoupled from α-methine proton.

In the CCl_4 solution the β-methylene-proton resonance of PMAVE overlapped with methyl-proton resonance, but in the pyridine solution it was partially separated from it as is shown in Fig. 2 (A). The β-methylene-proton resonance decoupled from the α-methine proton split into three peaks, at 1.96, 2.08, and 2.21 ppm (B in Fig. 2). These splittings are considered to be three of the four peaks of a typical AB quartet, which originated from the meso methylene protons of an isotactic polymer. The fourth peak at the highest field, must overlap with the methyl signal. These results suggest that the polymer obtained at −78°C was highly isotactic. On the other hand, the decoupled β-methylene resonances of the polymer obtained at 0°C in toluene (C in Fig. 2) was somewhat different, showing that the polymer was less isotactic and that the singlet due to the syndiotactic methylene protons overlaps with the peak at 1.96 ppm, one of the signals of the meso methylene quartet. However, no quantitative determination of the tacticity could be made because of the poor resolution of the decoupled spectrum.

NMR Spectra of PMAVE in Various Solvents. The NMR spectra of PMAVE obtained at −78°C in toluene were taken at 22.5°C on a 10 w/v% solution in various solvents. The results are shown in Table 1. All the signals shifted to a higher field on going from a CCl_4

Table 1. NMR spectra of PMAVE in various solvents at 22.5°C

Solvent	Chemical shift (ppm)					
	$-CH_2-\underset{\underset{O}{\vert}}{C}-$	$-C-\underset{\underset{O}{\vert}}{CH}-$	$\overset{\overset{O}{\vert}}{\underset{\underset{C}{\vert}}{CH_2}}$	$\overset{\vert}{\underset{\Vert}{C}}-CH_3$	$\overset{\vert}{\underset{\underset{CH_2}{\Vert}}{C}}-$	
Carbon tetrachloride	2.12	3.98	4.30	2.24	5.29	5.42
Benzene	1.54	3.56	3.67	1.49	4.64	4.91
Pyridine	1.56	3.54	3.66	1.43	4.57	4.82
Quinoline	1.96	3.87	3.95	1.69	4.86	5.16

solution to the solutions in aromatic solvents. The extent of the shift is almost the same in the benzene and pyridine solutions. The quinoline solution showed a smaller shift than the above two solutions did. While pyridine and quinoline have nearly the same dielectric constant and dipole moment, those of benzene are considerably smaller. The above results clearly indicate that the shifts are not caused by the different dielectric constants and dipole moments of the solvents, but by the interaction of the polymer with the solvents. The interaction may be the π-complex formation between the monomeric unit in PMAVE and the solvent molecule, as was reported in connection with the benzene solution of poly(methyl methacrylate).[13]

The temperature dependences of the chemical shifts were investigated in CCl_4 and quinoline solutions. In the CCl_4 solution the chemical shifts of all the protons were scarcely dependent at all upon the temperature. On the other hand, in the quinoline solution all the signals shifted to a low field with an increase in the temperature (Fig. 3). In the benzene and pyridine solutions, nearly the same changes in the chemical shifts were observed. These results may support the idea of the formation of a π-complex in these aromatic solvents.

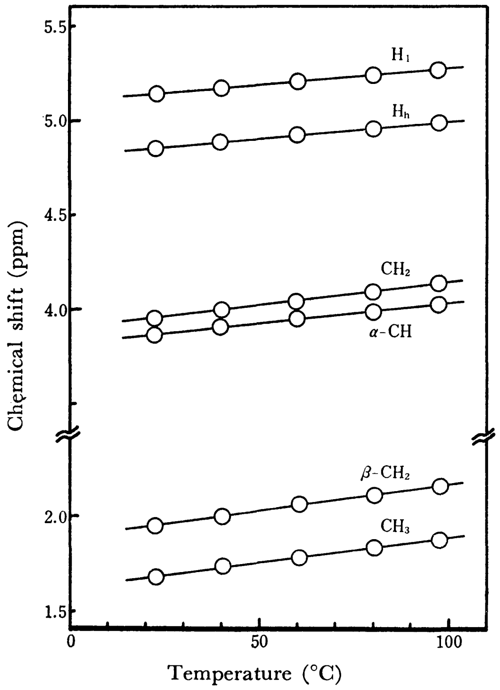

Fig. 3. Temperature dependences of the chemical shifts of all protons in PMAVE obtained in toluene at −78°C. ——Quinoline solution—— H_l and H_h denote the protons of vinyl methylene ones which give the signals at the lower and the higher field, respectively.

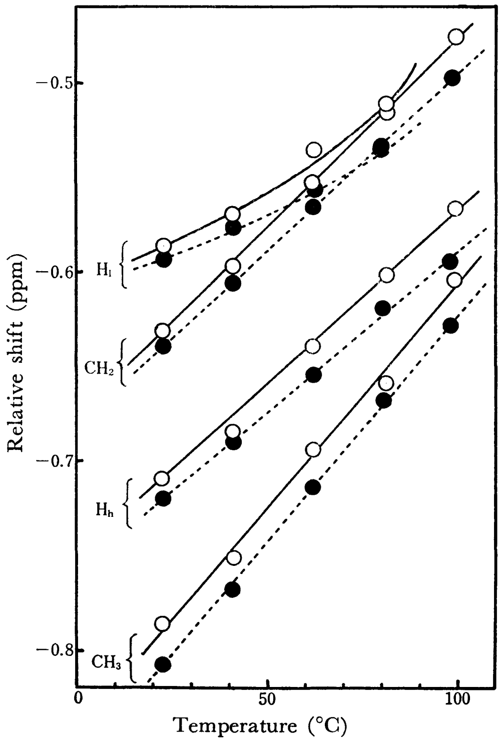

Fig. 4. Relative shifts of the protons in PMAVEs obtained in toluene at 0°C (○) and at −78°C (●) ——Pyridine solution——.

In Figs. 4 and 5 the relative shifts of the protons of the PMAVEs obtained at −78°C and 0°C in toluene are plotted against the temperature, where the relative shift is defined as the difference between the chemical shifts of each particular group in an aromatic solvent and in CCl_4. In both the pyridine (Fig. 4) and quinoline (Fig. 5) solutions, the relative shifts became smaller with an increase in the temperature. Small but significant differences were observed between the relative shifts of the PMAVE obtained at −78°C and those of the PMAVE obtained at 0°C in both the solutions.

Liu[14] has revealed, by NMR spectroscopy, that

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Table 2. Polymerization of MAVE in various solvents by $BF_3 \cdot OEt_2$
MAVE 16.8 mmol, $BF_3 \cdot OEt_2$ 0.2 mmol, Solvent 18 m*l*
Temp. −78°C, Time 24 hr.

No.	Solvent	Polymer yield (%)		
		Total	MeOH sol.	MeOH insol.
141	Toluene	56.9	5.8	51.1
68	CH_2Cl_2	13.7	13.7	trace
173	$EtNO_2$	trace	trace	0
145	Et_2O	0	0	0
169	Heptane + Toluene (2 : 7)[b]	58.1	8.6	49.5
165	Heptane + Toluene (1 : 1)[b]	76.3	15.6	70.7
168	Heptane + Toluene (7 : 2)[b]	81.5	14.0	67.5
166	Heptane	35.7	16.8	18.9[a]

a) Insoluble in usual organic solvent b) Volume ratio

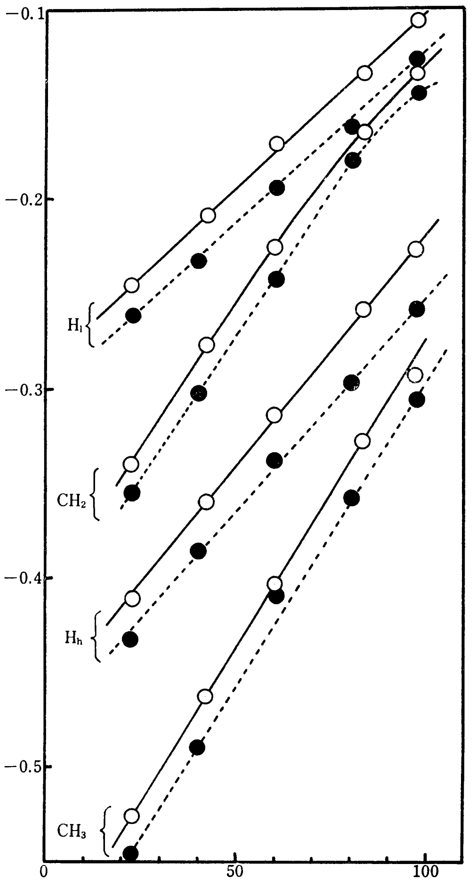

Fig. 5. Relative shifts of the protons in PMAVEs obtained in toluene at 0°C (○) and at −78°C (●) ——Quinoline solution——.

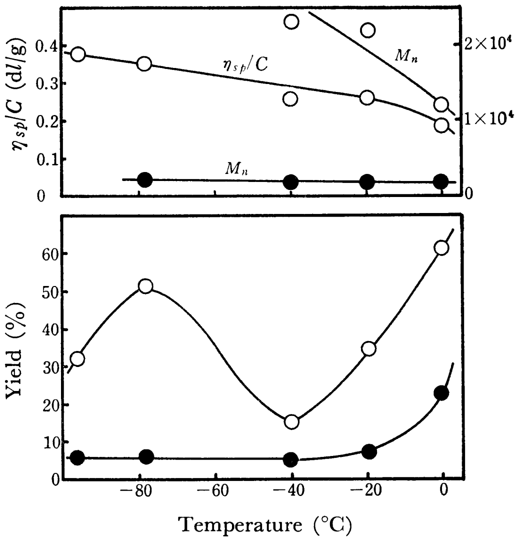

Fig. 6. Polymerization of MAVE in toluene by $BF_3 \cdot OEt_2$ for 24 hrs at various temperatures.
○: Methanol insoluble polymer, ●: Methanol soluble polymer. MAVE 16.8 mmol, toluene 18 m*l*, $BF_3 \cdot OEt_2$ 0.20 mmol.

the tacticity variation affects the polymer-solvent interaction in a benzene solution of poly(methyl methacrylate). Therefore, the results presented above indicate that the tacticity of PMAVE obtained at −78°C in toluene is different from that of PMAVE obtained at 0°C, as has been suggested above.

Effect of the Polymerization Temperature. The polymerizations were carried out in toluene at various temperatures. The results are shown in Fig. 6. The yield of the methanol-soluble polymer was constant below −20°C and increased remarkably at 0°C. However, the molecular weight was almost constant, regardless of the polymerization temperature.

The yield of the methanol-insoluble polymer had its minimum at −40°C. The solution viscosity and the molecular weight of the methanol-insoluble polymer decreased slightly with the elevation of the polymerization temperature. The polymer obtained below −78°C was a white powder which had an isotactic configuration, as has been mentioned above. The polymer obtained at 0°C was a viscous liquid which had a molecular weight of 12000. The rate of the termination or chain-transfer reaction in the polymerization may increase, and a polymer with a lower molecular weight may be obtained with an increase in the polymerization temperature.

Polymerization in Various Solvents. The polymerizations were carried out in various solvents at −78°C. The results are listed in Table 2. The yield of the polymer was lowered in polar solvents, and no methanol-insoluble polymer was obtained.

In *n*-heptane-toluene mixtures, the yields of the methanol-insoluble polymer were much higher than in toluene or *n*-heptane alone. In *n*-heptane, the yield of the polymer decreased and a part of the polymer obtained was insoluble not only in methanol but also in usual organic solvents, probably because of cross-linking during the polymerization reaction.

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